

COLOUR AND CHEMICAL CONSTITUTION.

PART XVII.—THE AZO DYES AND OTHER MONOCYCLIC COLOURS.

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Some preliminary work on the azo dyes appears in Part XII of this work, pp. 215–216, accompanied by the remark that the problem appeared hopeless of solution. Since then, by examining all the related simpler substances, I have discovered a method of calculating their colours, and thus uniting them to the monocyclic class already discussed in Part XIII.

The examination of the simpler substances could only be done by photography. Other colour chemists will therefore join me in thanking Mr. E. R. Grills (of Hortor's Ltd., Johannesburg), who presented me with a diffraction-grating specially mounted on a thin cover-glass such as is used in microscopy: this instrument enabled me to photograph down to λ 320 and thus find the absorption of many colourless substances which required to be examined in order to discover the theory of the azo dyes. The fact that I had to use a glass (not quartz) lens prevented a complete investigation further down in the ultra-violet. This I hope to attack later on.

Remarkable to say, the very first photograph I took with the new apparatus gave a discovery. Alkaline paraoxazobenzene in water was the substance the spectrum of which was photographed, and the negative showed not one broad band at λ 420, as previously supposed from visual observation (Tuck, J.C.S., London, 1907, diagram on p. 450, and Moir, *loc. cit.*), but *two* distinct although overlapping bands at $\lambda\lambda$ 433 and 395. Further investigation showed that *all* the members of the family show this phenomenon: sometimes, as in acid butter-yellow, both bands are very distinct, and sometimes they are so overlapped that only a faint luminosity appears in the middle and the band looks at first like a single very broad one; in such cases the estimate of the centres of the two bands is quite uncertain, being in doubt by more than five units.

Again, all the substances are indicators and change colour if made acid or alkaline, thus giving three kinds of spectrum according to the

reaction of the water in which they are examined. As all the absorption-bands are double, each substance has six bands in all, and it is the object of this paper to calculate all the six bands of each substance.

This leads to the result that each of the six bands corresponds to a different chemical constitution, or at least to a different orbital motion of an electron round the molecule.

As examples, *p*-oxyazobenzene has $\lambda\lambda$ 433 and 395 when alkaline, $\lambda\lambda$ 490 and 463 when acid, and $\lambda\lambda$ about 340 and 315 when neutral, the corresponding figures for butter-yellow being $\lambda\lambda$ 490+460 and 543+508 and about 405+375. Taking the former example, the six chemical constitutions are respectively: Ph . NH . NOH . C₆H₄O', Ph . NOH . NH . C₆H₄O', Ph . NHCl : N . C₆H₄OH, Ph . N : NHCl . C₆H₄OH, Ph . NH . N : C₆H₄ : O, Ph . N : N . C₆H₄OH.

SOLUTION OF THE PROBLEM OF THE OXY-COMPOUNDS.

Let phenate-ion, C₆H₅O' have λ 287 in water.*

Let the α -methylene-interposition-colour-factor, -CH₂-, be 0.92.

Let the α -imino- " " " -NH-, be 1.09.

Let the β -methylene- " " " . be 1.15.

Let the β -imino- " " " . be 1.22.

Let the α -oxidation-factor be 1.10.

Let the β - " " " 1.035.

Let the α -phenyl-substitution-factor be . . . 1.135.†

Let the β - " " " " . . . 1.03.

Then we have all the data for calculating the bands of the oxy-compounds of azobenzene, azomethine, stilbene, benzaldehyde, benzhydrol, benzophenone, diphenylamine, triphenylcarbinol, phenylhydroxylamine, etc.

The method of calculation is, as before, factorial. All the relative factors taken from the formula of the substance are multiplied together, the result being the wave-length of the band-centre corresponding to that formula. For example, Ph NH NOH C₆H₄O' gives:—

287 (phenate) $\times$ 1.09 (α -imino) $\times$ 1.10 (α -oxidation) $\times$ 1.22 (β -imino) $\times$ 1.03 (β -phenyl), which equals 432.4, the decimal part having no significance on account of the factors being correct only within one-half per cent.

In order to simplify the subsequent calculations, some of the factors may be multiplied together to begin with, thus giving useful subsidiary factors.

Thus: α -carbinol, CHOHa, = 0.92 $\times$ 1.10 = 1.01

β - " CHOH β , = 1.15 $\times$ 1.035 = 1.19

* Observation agrees with this.

† As found before in Part XIII, A, of table on p. 36.

α -oximino, $\text{NOH}\alpha$,	$= 1.09 \times 1.10 = 1.20$
β - „ „ $\text{NOH}\beta$,	$= 1.22 \times 1.035 = 1.26$
β -benzyl, PhCH_2	$= 1.15 \times 1.03 = 1.185$
β -Ph . CHOH	$= 1.19 \times 1.03 = 1.23$
β -anilino, PhNH	$= 1.22 \times 1.03 = 1.255$
β -Ph . NOH	$= 1.26 \times 1.03 = 1.30$

The above example, one of the bands of alkaline *p*-oxyazobenzene, now becomes : $287 (\text{phenate}) \times 1.20 (\alpha\text{-oximino}) \times 1.255 (\beta\text{-anilino}) = 432\frac{1}{2}$. The other band, from the formula $\text{Ph NOH NH C}_6\text{H}_4\text{O}'$ is got from : $287 \times 1.09 (\alpha\text{-imino}) \times 1.30 (\beta\text{-phenyloximino}) = 407$. The former agrees exactly with observation, but the latter is a little too high. The reason why the spacing and overlapping of the pair of bands varies has not been discovered.

We will now proceed to calculate all the oxy-compounds, beginning with the simplest.

1. The $\alpha\text{-CH}_2$ group put into phenate gives *p*-cresolate : calculated λ 264 (or 287×0.92). Not observed in water, λ about 285 in alcohol (Baly and Ewbank).

2. The $\alpha\text{-CH}_2$ group taken out of quinomethane gives ionised quinol : calculated λ $315\frac{1}{2}$ (or $290 \div 0.92$) for $\text{HO C}_6\text{H}_4\text{O}'$: alternatively phenate $\times$ oxidation-factor 1.1 : not observed.

The following table exhibits the rest of the results :—

Name.	Basis of Calculation.	Calculated λ .	Observed λ .
<i>p</i> -oxybenzaldehyde . .	Quinol $\times \text{CHOH}\alpha$. .	319	330 (alc.).
<i>p</i> -oxybenzophenone . .	Foregoing $\times \text{Pha}$. .	362	Agrees visually.
<i>p</i> -oxybenzylalcohol . .	Phenate $\times \text{CHOH}\alpha$. .	290	See Part XIII.
<i>p</i> -oxybenzhydrol . .	Foregoing $\times \text{Pha}$. .	329	„
Fuchsone . .	Foregoing again $\times \text{Pha}$. .	374	380 (alc.).
<i>p</i> -oxydiphenylmethane . .	Cresolate $\times \text{Pha}$. .	300	
<i>p</i> -oxytriphenylmethane . .	Foregoing $\times \text{Pha}$. .	340	
<i>p</i> -aminophenol . .	Phenate $\times \text{NH}\alpha$. .	313	
Quinone-imine . .	„ $\times \text{NOH}\alpha$. .	344	About 355 (ether).
Quinone-anile . .	Foregoing $\times \text{Pha}$. .	390	Agrees visually.
<i>p</i> -oxydiphenylamine . .	Aminophenol $\times \text{Pha}$. .	355	
Quinone-oxime . .	Quinol $\times \text{NOH}\alpha$. .	379	397 (NaOH aqueous).
<i>p</i> -oxyazobenzene A . .	Phenate $\times \text{NOH}\alpha \times \text{PhNH}\beta$	432	433.
„ B . .	„ $\times \text{NH}\alpha \times \text{PhNOH}\beta$	407	395.
<i>p</i> -oxybenzalaniline A . .	„ $\times \text{CHOH}\alpha \times \text{PhNH}\beta$	364	About 375.
„ B . .	„ $\times \text{CH}_2\alpha \times \text{PhNOH}\beta$	343	About 345.
<i>p</i> -benzalaminophenol A . .	„ $\times \text{NOH}\alpha \times \text{PhCH}_2\beta$	407	400.
„ B . .	„ $\times \text{NH}\alpha \times \text{PhCHOH}\beta$	384	About 375.
<i>p</i> -oxystilbene A . .	„ $\times \text{CH}_2\alpha \times \text{PhCHOH}\beta$	323	} 329 not separated.
„ B . .	„ $\times \text{CHOH}\alpha \times \text{PhCH}_2\beta$	344	

In addition the monocyclic phthaleins may be calculated, using the CO_2H factor of Part XIII: the results are the same as in Part XIII and agree with observation. Other unobserved but calculated substances are: $\text{PhCH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{O}'$ (calc. λ 356), $\text{Ph} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{O}'$ (calc. λ 447),

$\text{Ph}_2\text{N} \cdot \text{CHOH} \cdot \text{C}_6\text{H}_4\text{O}'$ (calc. λ 375), and $\text{Ph}_2\text{C} : \text{CH} \cdot \text{C}_6\text{H}_4\text{O}'$ (calc. λ 339 double). Almost all the possible substances have thus been considered.

Note.—The bands of the *acid* solutions of the oxyazo and oxyazomethine dyes are calculated * by multiplying the above-calculated (alkaline phase) bands by the factor 1.13, and the bands of the *neutral* phase by multiplying by a factor which is about 0.8. All the six bands of each substance are thus calculated.

MONOCYCLIC AMINO-COMPOUNDS.

The calculation of these is simply made from the oxy-compounds by multiplying by the factor 1.18 for acid solutions, the factor for $\frac{\text{NH}_3\text{A}}{\text{OK}}$.

For neutral solutions the factor $\frac{\text{NH}_2}{\text{OK}}$ is about 1.05.

TABLE OF CALCULATED AMINO-COMPOUNDS (ACID).

Name.	Calculated λ .	Observed λ .
<i>p</i> -toluidine salt . . .	$264 \times 1.18 = 312$	
<i>p</i> -aminobenzaldehyde . . .	377	Agrees visually.
<i>p</i> -aminobenzophenone . . .	427	Probably exceptional.
Aminobenzylalcohol . . .	342	} See Part XIII.
Aminobenzhydrol . . .	388	
Fuchsonium salts . . .	440	430.
Aminotriphenylmethane . . .	401	
<i>p</i> -phenylenediamine . . .	370	
Quinone-diimine . . .	405	About 370 (ether).
Aminodiphenylamine . . .	420	
Quinone-phenyldiimine . . .	460	488 and 450.
<i>p</i> -nitrosoaniline . . .	448	410 vague.
Aniline yellow A . . .	512	520.
„ B . . .	480	485.
Aminobenzalaniline A . . .	430	About 440.
„ B . . .	405	About 415.
Benzalphenylenediamine A . . .	480	} 465 broad, probably double.
„ B . . .	453	
<i>p</i> -aminostilbene A . . .	381	
„ B . . .	405	
Amino-azoxybenzene . . .	527	

* See the Table at the end for the observations.

MONOCYCLIC DIMETHYLAMINO-COMPOUNDS.

The multiplying factor for $\frac{\text{NMe}_2\text{HA}}{\text{OK}}$ is 1.25, *i.e.* for acid solutions. For the neutral phases the factor is 1.13, *i.e.* the bands of a *neutral* dimethylamino substance are practically the same as those of the corresponding oxy substance examined in *acid* solution (see previous page).

TABLE OF CALCULATED DIMETHYLAMINO-COMPOUNDS (ACID).

Name.	Calculated λ .	Observed λ .
Dimethyl- <i>p</i> -toluidine . . .	330	
<i>p</i> -dimethylaminobenzaldehyde . . .	399	About 380 and 355.
Dimethylaminobenzophenone . . .	452	Probably exceptional.
Dimethylaminobenzhydrol . . .	411	About 405.
Dimethylaminobenzyl alcohol . . .	363	
Dimethylfuchsonium salts . . .	466	460.
Dimethylaminotriphenylmethane . . .	425	
Dimethyl- <i>p</i> -phenylenediamine . . .	392	
Dimethyl-quinonedimine . . .	429	About 400.
Dimethylaminodiphenylamine . . .	445	
Dimethylphenylquinonedimine . . .	488	
Nitrosodimethylaniline . . .	474	457.
Butter-yellow A . . .	542	543.
„ B . . .	509	508.
Dimethylaminobenzalaniline A . . .	508	513.
„ B . . .	480	482.
Benzaldimethylphenylenediamine A . . .	455	460.
„ B . . .	430	427.
Dimethylaminostilbene A . . .	430	
„ B . . .	403	375.
Dimethylaminoazoxybenzene . . .	559	
Dimethylamino-stilbeneoxide . . .	445	
Dimethylamino-benzophenoneanile . . .	524	

There are still many blanks in the observations, it being almost impossible for one investigator to repeat all the work which has stretched over the last thirty-five years ; but the calculations cover nearly all the possible monocyclic compounds of this class.

Quinone Compounds.—Quinone in water has a band at λ 455 or 460 (centre vague), but cannot be observed in alkaline solution, *i.e.* as $\text{HO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 : \text{O}'$ on account of oxidation. Assuming, however, that the water solution is ionised, we calculate the α -*oxo-interposition factor* to be about $457 \div 315\frac{1}{2}$ (quinol) or 1.45.

Quinonedioxime (in excess NaOH, as it is a very weak acid) has a sharp, strong band at λ 366, and quinonemonoxime in alkali a band which is

roughly intermediate between those of quinone and its dioxime. This gives a ratio $O:NOH$ of 1.15 experimentally, whereas the ratio $-O-/-NOH-$ is $1.45 \div 1.2$ or 1.21. Alternatively, quinonedioxime calculated from $HO-NOH \cdot C_6H_4 \cdot NOH \cdot H$, or from $NO \cdot C_6H_4 \cdot HNOH$, should have λ 412 instead of λ 366, so that it is necessary to make some distinction between the two groups attached to the benzene ring.

The old terms *chromophore* and *chromogen* involve two elements and a double bond and are now out of date, since, as I have shown in the first paper of this series, colour may arise merely from the attachment of two groups to a ring, the whole being oxidised.

I propose the new term *hapton* * for the second element and its attachments, reserving the old term *auxochrome* for OH , NH_2 , $NHAlk$, and $NAlk_2$ restrictively. The *hapton* is intended to be a general term for C, N, O, or S.

Such a substance as sodium phenate, consisting of a ring and an auxochrome but no hapton, has not a strong absorption visible in great dilution (say $N/40,000$) as the true colouring-matters have. Technically it is a *coloured substance* with an absorption-band in the ultra-violet. Its pentabromo substitution-product is yellow, the 'loading' having raised the absorption-band from λ 287 to about λ 365, but the absorption-band is still not strong.

Now let a hapton be added, giving in the unoxidised condition $CH_3C_6H_4O'$, $NH_2 \cdot C_6H_4 \cdot O'$, $HO \cdot C_6H_4 \cdot O'$, $SH \cdot C_6H_4 \cdot O'$. These still remain *coloured substances*, not *colouring-matters*. They are leuco-compounds, with only shallow absorption.

Parahydroxybenzaldehyde is the simplest true *colouring-matter* giving a strong, sharp absorption-band even in high dilution. We thus require for a colouring-matter a ring, an auxochrome, and a hapton, and the whole must be oxidised. It is best to adopt an agnostic attitude as to the nature of the oxidation. The formula $HO \cdot C_6H_4 \cdot CHO$ refers to solid neutral hydroxybenzaldehyde, but the coloured aqueous alkaline solution may be $O' \cdot C_6H_4 \cdot CHO$, $O : C_6H_4 : CHO'$, $O \cdot C_6H_4 \cdot CHO'$ and half a dozen other formulæ involving the valencies of the ring itself.

Apparently the relation of the hapton to the auxochrome may be either ortho, meta, or para, but the bands of meta-compounds appear to be less pronounced.

The term *dye* is restricted to colouring-matters which stick to fabrics or mordants, e.g. phenolphthalein is not a dye.

* Cf. haptophore in bacteriology.

MISCELLANEOUS OBSERVATIONS ON AZO-DYES AND AZOMETHINES.

1. Ortho-hydroxyazobenzene (alkali)	. . .	$\lambda\lambda$ 441 and 390.
2. " " (acid)	. . .	λ 480 broad single.
3. Para- " "	. . .	λ 475 broad = $\lambda\lambda$ 491+460 in weaker acid.
4. CH ₃ -der. of (1) = benzeneazo- <i>p</i> -cresol (alkali)	. . .	λ 493 broad single.
5. SO ₃ K- " " = " <i>p</i> -phenolsulphonate	. . .	λ 455 " "
6. 2-4-6-tribromobenzeneazophenol (alkali)	. . .	$\lambda\lambda$ 430+384.
7. Benzeneazo- <i>o</i> -bromophenol	" . .	$\lambda\lambda$ 436+390.
8. 2-nitrobenzeneazophenol	" . .	$\lambda\lambda$ 487+440.
9. 4- " "	" . .	λ 490 broad single.
10. 4-nitrobenzeneazo- α -naphthol	" . .	λ 576 broad = $\lambda\lambda$ 602+552.
11. Foregoing in alcoholic alkali	. . .	λ 598 " = $\lambda\lambda$ 623+572.
12. No. 9 in " "	. . .	λ 502 " = $\lambda\lambda$ 540+490.
13. 4-sulphobenzeneazophenol (alkali)	. . .	λ 440 and ? 400.
14. 4-bromo- " " "	. . .	$\lambda\lambda$ 445+395.
15. 4-ethoxy- " " "	. . .	$\lambda\lambda$ 447+390.
16. 4-sulphobenzeneazo- <i>o</i> -cresol	" . .	λ 463 single.
17. 4- " " -m- " "	. . .	λ 475 " "
18. Benzeneazoguaiacol	" . .	λ 460 broad single.
19. Benzeneazothymol	" . .	$\lambda\lambda$ 455+410.
20. " - α -naphthol	" . .	λ 496 broad single.
21. 4-sulphobenzeneazo- α -naphthol (alkali)	. . .	λ 513 " "
22. Benzeneazo-tetrahydro- α - " "	. . .	$\lambda\lambda$ 470+430.
23. " -catechol	" . .	$\lambda\lambda$ 480+430.
24. 4-diphenylazophenol	" . .	λ 451.
25. Diphenyltetrazo- <i>p</i> -phenolsulphonate (alkali)	. . .	λ 475 broad single.
26. 4-NO ₂ C ₆ H ₄ CH : NC ₆ H ₄ OH	" . .	λ 455 " "
27. 4-NO ₂ C ₆ H ₄ N : CHC ₆ H ₄ OH	" . .	λ about 410.
28. 4-NO ₂ C ₆ H ₄ CH : NC ₁₀ H ₆ OH α	" . .	$\lambda\lambda$ 560+505 in alcohol.
29. 4-NO ₂ C ₆ H ₄ N : CHC ₁₀ H ₆ OH α	" *	$\lambda\lambda$ 510 (+545 faint) in alcohol.
30. 4-diphenylazonaphthionic acid (in HCl)	. . .	λ 575 broad single.
31. Congo-red (in HCl)	. . .	λ 580 " "

From these we infer (1) that the ordinary substitutions have about the same small effect as in the dicyclic series : paranitro and naphthyl have the largest factors = 1.16 and 1.19 respectively ; (2) the benzidine dyes are practically the same as the diphenyl dyes, *i.e.* only half the molecule acts.

* I have to thank Professor G. T. Morgan for this specimen (J.C.S., 1922, p. 5).